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COMPOSITION FOR USE AS A REINFORCING FILLER IN POLYMERCOMPOSITIONS

The present invention relates to a composition, able to be used as a reinforcing filler in polymer compositions, which is obtained by drying a suspension containing particles having a form factor of less than 15 and particles dispersible in a polymer medium.

It also relates to the polymer compositions containing this composition.

Finally, it furthermore relates to the finished articles based on these polymer compositions.

It is known to employ white reinforcing fillers in polymers, in particular in elastomers, especially precipitated silica.

In general, it is known that to obtain the optimum reinforcing properties provided by a filler, it is necessary for the latter to be present in the polymer matrix in a final form which is both as finely divided as possible and distributed as homogeneously as possible. However, such conditions can be achieved only when, on the one hand, the filler is very easily incorporated into the matrix during blending with the polymer (incorporability of the filler) and very easily deagglomerated in the form of a very fine powder (deagglomeration of the filler) and when, on the other

hand, the powder resulting from the aforementioned deagglomeration process is, in turn, itself perfectly and homogeneously dispersed in the polymer (dispersion of the powder).

In addition, for reasons of mutual affinities, the filler particles may have an annoying tendency in the elastomer matrix to agglomerate with one another. These filler/filler interactions have the undesirable consequence of limiting the reinforcing properties to a level substantially below that which would theoretically be possible to achieve if all the polymer/filler interactions capable of being created during the blending operation were actually to be obtained.

Furthermore, such interactions tend, in the green state, to increase the stiffness and the consistency of the mixes, thus making them more difficult to process.

For some time, precipitated silica dispersible in a polymer medium, that is to say having a high dispersibility in its application medium, has in particular been used.

Combinations of fillers, obtained by direct blending of each of the fillers in solid form, for example alumina and dispersible precipitated silica, may also be used. However, the limited dispersibility of one of the fillers in the application medium again

crops up when using the combination and the reinforcing properties of the polymer compositions obtained are not always satisfactory: agglomerated objects, possibly up to about ten microns in diameter approximately, are observed in these polymer compositions into which additives have thus been incorporated, agglomerates which are deleterious to the properties of these compositions.

It is an object of the invention to provide a composition which is prepared in a particular way from at least two components, one of them being dispersible in the polymer medium and the other preferably not being dispersible in such a medium, and which, used as a filler in polymer compositions, achieves, in the latter, a very satisfactory compromise between mechanical, rheological and dynamic properties, and which, above all, provides these polymer compositions with improved properties over those obtained using, as filler, the direct blend of each of the components in solid form.

For this purpose, the present invention provides a composition obtained by drying a suspension (in general an aqueous suspension) containing, on the one hand, mineral or organic particles A having a form factor of less than 15 and, on the other hand, mineral or organic particles B dispersible in a polymer medium.

In general, the composition according to the

invention is prepared by drying a suspension obtained by mixing at least one suspension (in general an aqueous suspension) of mineral or organic particles A having a form factor of less than 15 with at least one suspension (in general an aqueous suspension) of organic or mineral particles B dispersible in a polymer medium; in other words, the composition according to the invention is in general prepared by co-drying the two suspensions of particles, A and B.

Each of these two suspensions may be used in the form of a suspension directly resulting from the process for preparing particles A or B.

Each of these two suspensions may also have been obtained by redispersing particles A or B in solid form (dry form) in a liquid medium. Particles A and/or B may have undergone beforehand, at least partially, a surface treatment.

It may be preferable for the mixing of the two suspensions to comprise a homogenization operation or a treatment allowing the particles to deagglomerate, such as, for example, wet milling or, for example, an ultrasonic treatment; in general, this homogenization operation consists of mechanical stirring.

A stabilizer, for example a hydrocolloid, may also be added during the mixing.

The drying (or co-drying) operation may be carried out using any means known per se.

However, according to a highly advantageous embodiment of the invention, the drying is carried out by spraying (co-spraying), that is to say by spraying the suspension in a hot atmosphere (spray drying). The composition according to the invention can therefore be referred to as the "co-sprayed material". The outlet temperature of the atomizer employed is usually less than 170°C, preferably less than 140°C and is, for example, between 100 and 135°C. The drying may be carried out by means of any type of suitable atomizer, especially a turbine atomizer with nozzles; preferably, a nozzle atomizer, in particular with liquid pressure, is employed.

According to the invention, the composition obtained after the drying operation is in solid (dry) form. It may be, particularly when the drying has been carried out by means of a nozzle atomizer, in the form of approximately spherical beads, the mean size of which may be at least 80  $\mu\text{m}$ , in particular at least 100  $\mu\text{m}$ , for example at least 150  $\mu\text{m}$ ; this size is in general at most 300  $\mu\text{m}$ . The mean size is measured according to the NF X 11507 (December 1970) standard by dry screening and by determining the diameter corresponding to a 50% cumulative oversize.

After the drying operation, the composition obtained may, if so desired, undergo a milling step or another forming step such as, for example a

granulation, compaction or extrusion step.

The mineral or organic particles A and B used initially to prepare the composition according to the invention are dispersible in the suspension medium, possibly, if necessary, by using an additive or a post-treatment aid to dispersion.

The mineral or organic particles A have a form factor, defined as being the ratio of the largest mean dimension of particles A to the smallest mean dimensions of particles A, of less than 15, in particular at most 12.

In general, particles A have a mean aggregate size of less than 1  $\mu\text{m}$ , in particular less than 0.8  $\mu\text{m}$ , for example less than 0.5  $\mu\text{m}$ .

Particles A used initially to prepare the composition according to the invention are preferably mineral particles.

These particles A may thus be aluminosilicate or titanium dioxide particles.

These particles A may also be aluminum or magnesium hydroxycarbonate, hydroxyoxycarbonate or oxycarbonate particles, or hydrotalcite particles.

Preferably, particles A are alumina particles.

According to a variant of the invention, this alumina may especially be obtained by autoclaving a suspension of boehmite, or preferably pseudo-boehmite,

especially in the presence of at least one acid, particularly acetic acid (with, for example, an acetic acid/ $\text{Al}_2\text{O}_3$  molar ratio of between 1.5 and 5, in particular between 2 and 4). In general, the autoclaving is then carried out at a temperature hold of between 110 and 150°C, the said hold lasting from 6 to 10 hours. Optionally, this autoclaving may be followed by a chemical and/or thermal post-treatment (neutralization or calcination, for example).

According to another variant of the invention, this alumina is a crystalline monohydrate, essentially in boehmite form, obtained by coprecipitating sodium aluminate and aluminum sulfate.

Particles A used initially to prepare the composition according to the invention are generally not dispersible in the application medium, that is to say in a polymer medium, unlike particles B. However, it has been found that, surprisingly, because of the way in which the composition according to the invention is prepared, the dispersibility of particles A when this composition is used as a filler in a polymer composition was in general substantially improved; thus it has been found that, in a photograph obtained by scanning electron microscopy, no or only very few agglomerates or aggregates are detected in the polymer composition into which additives have been incorporated in this way, whereas a substantial amount of



agglomerated objects, possibly reaching about ten microns in diameter approximately, is observed in the case of the polymer composition containing, as filler, the direct blend of particles A and particles B in solid form; the quality of the macrodispersion of particles B, especially in the case of alumina, in the rubber composition may thus be substantially improved.

Particles B used initially to prepare the composition according to the invention are dispersible in a polymer medium, that is to say they have a high dispersibility in their application medium.

In the context of the invention, particles A and particles B are of different chemical nature (for example, if particles A are titanium dioxide particles then particles B are not formed from titanium dioxide (identical or not identical to that forming particles A)).

Preferably, particles B consist of precipitated silica particles having a high dispersibility in a polymer medium, in particular in elastomers.

As indicated above, these precipitated silica particles, having a high dispersibility in elastomers may be used to prepare the composition according to the invention in the form of a suspension coming directly from the process for preparing them. They may also be used by redispersing them in a medium after they have



been prepared in solid form.

Among suitable precipitated silicas, mention may be made of those described in or obtained by the processes indicated in applications EP 0 520 862, WO 95/09127 and WO 95/09128.

For example, precipitated silica particles may be chosen, for example in the form of approximately spherical beads, especially having a mean size of at least 80  $\mu\text{m}$ , having a pore distribution such that the pore volume formed by the pores whose diameter is between 175 and 275 Å represents at least 50% of the pore volume formed by the pores having diameters of less than or equal to 400 Å.

Precipitated silica particles may also be chosen which have an ultrasonic deagglomeration factor ( $F_D$ ) of greater than 5.5 ml and a median diameter ( $\phi_{50}$ ) after ultrasonic deagglomeration of less than 5  $\mu\text{m}$ ; preferably, said precipitated silica particles then furthermore have a pore distribution such that the pore volume formed by the pores whose diameter is between 175 and 275 Å represents less than 50% of the pore volume formed by the pores having diameters of less than or equal to 400 Å.

It is also possible to choose precipitated silica particles having an ultrasonic deagglomeration factor ( $F_D$ ) of greater than 11 ml and a median diameter ( $\phi_{50}$ ) after ultrasonic deagglomeration of less than

2.5  $\mu\text{m}$ .

The pore volumes are measured by mercury porosimetry; the preparation of each specimen takes place as follows: each specimen is predried for 2 hours in an oven at 200°C, then placed in a test chamber within 5 minutes of being removed from the oven, and vacuum-degassed, for example using a rotary vane pump; the pore diameters are calculated from the Washburn equation with a contact angle  $\theta$  of 140° and a surface tension  $\gamma$  of 484 dynes/cm (MICROMERICS 9300 porosimeter).

The dispersibility of the precipitated silicas is evaluated by means of the test carried out according to the following protocol:

The cohesion of the agglomerates is assessed by a particle size measurement (by laser diffraction) carried out on a suspension of silica ultrasonically deagglomerated beforehand; in this way, the deagglomerability of the silica is thus measured (break-up of objects 0.1 to a few tens of microns in size). The ultrasonic deagglomeration is carried out by using a VIBRACELL BIOBLOCK (600 W) sonificator fitted with a probe 19 mm in diameter. The particle size measurement is carried out by laser diffraction using a SYMPATEC particle size analyzer.

Two grams of silica are weighed out in a pill box (height: 6 cm and diameter: 4 cm) and topped up to

50 grams by adding deionized water; a 4% aqueous suspension of silica is thus produced, which is homogenized for 2 minutes by magnetic stirring. Next, the ultrasonic deagglomeration operation is carried out as follows: with the probe immersed over a length of 4 cm, the output power is adjusted so that the needle of the power dial is deflected to the point indicating 20%. The deagglomeration is carried out for 420 seconds. Next, the particle size measurement is carried out after having put a known volume (expressed in ml) of the homogenized suspension in the container of the particle size analyzer.

The value of the median diameter  $\phi_{50}$  obtained is lower, the higher the dispersibility/deagglomerate ability of the silica. The ratio  $(10 \times \text{volume of suspension introduced (in ml)}) / (\text{optical density of the suspension detected by the particle size analyzer})$ , this optical density being around 20, is also determined. This ratio is an indicator of the content of particles having a size smaller than  $0.1 \mu\text{m}$ , which are not detected by the particle size analyzer. This ratio, called the ultrasonic deagglomeration factor ( $F_D$ ), is higher, the higher the dispersibility/deagglomerability of the silica.

The precipitated silica particles able to be used within the context of the invention may have a CTAB specific surface area of between 50 and  $240 \text{ m}^2/\text{g}$ ,

preferably between 100 and 240 m<sup>2</sup>/g and in particular between 140 and 240 m<sup>2</sup>/g; it may thus be between 140 and 200 m<sup>2</sup>/g, for example between 140 and 170 m<sup>2</sup>/g. The CTAB specific surface area is the external surface area determined according to the NF T 45007 (November 1987) (5.12) standard.

To prepare the composition according to the invention, the amount of particles B used represents from 0.1 to 99.9% and, especially when particles B are precipitated silica particles, preferably from 50 to 98%, for example 60 to 85%, by weight with respect to the total amount of particles A and B used.

One particularly advantageous application of the composition according to the invention is as a reinforcing filler in the polymer compositions. It achieves, in the latter, a very satisfactory compromise between mechanical, rheological and dynamic properties and, above all, these properties are improved over those obtained using the direct blend of particles A and particles B in solid form as filler.

The polymer compositions in which the composition according to the invention is used as reinforcing filler, and which constitute a further subject matter of the invention, are in general based on one or more polymers or copolymers, in particular on one or more elastomers (especially thermoplastic elastomers), preferably having a glass transition

temperature of between  $-150$  and  $+300^{\circ}\text{C}$ , for example between  $-150$  and  $20^{\circ}\text{C}$ .

As possible polymers, mention may be made, in particular, of diene polymers, in particular diene elastomers.

For example, mention may be made of natural rubber, polymers or copolymers deriving from aliphatic or aromatic monomers containing at least one unsaturated group (such as, especially, ethylene, propylene, butadiene, isoprene and styrene), polybutyl acrylate, or combinations thereof; mention may also be made of silicone elastomers and halogenated polymers.

The polymer (copolymer) may be a bulk polymer (copolymer), a polymer (copolymer) latex or a polymer (copolymer) solution in water or any other suitable dispersing liquid.

Said polymer compositions may be sulfur-vulcanized.

In general, they furthermore include at least one coupling agent and/or at least one recovery agent; they may also include *inter alia* an antioxidant.

Advantageously, they include no reinforcing fillers other than the composition according to the invention.

The proportion by weight of the composition according to the invention in the polymer composition may vary over quite a wide range. In general, it

represents from 25 to 70%, for example 35 to 60% of the amount of polymer(s).

The present invention also relates to the finished articles based on the polymer compositions described above. Mention may be made, as finished articles, of floor coverings, shoe soles, vehicle track parts, tire covers (particularly tire treads and sidewalls), cablecar rollers, seals for domestic electrical appliances, sheaths, cables and transmission belts.

The following examples illustrate the invention without, however, limiting the scope thereof.

#### EXAMPLE 1

A suspension having an  $\text{Al}_2\text{O}_3$  content of 64 g/l was formed by mixing 250 g of pseudo-boehmite (obtained by the coprecipitation of sodium aluminate and aluminum sulfate and having an  $\text{Al}_2\text{O}_3$  solids content of 70%) with 2.7 liters of water. This suspension was stirred by means of a mechanical stirrer (Rayneri Turbo test 200) at a speed of 2000 revolutions per minute, for 20 minutes. The pH of the suspension was then 7.9.

Next, 309 g of acetic acid were added and the stirring continued for 20 minutes. The final pH was 2.9 and the final volume was 3 liters. The acetic acid/ $\text{Al}_2\text{O}_3$  molar ratio was 3.

The suspension obtained was placed in a glass

autoclave having a capacity of 5 liters and subjected to an autoclaving operation under the conditions below:

- stirring speed: 560 rpm;
- temperature rise time: 1 hour;
- temperature hold: 130°C;
- hold time: 8 hours.

After this autoclaving operation, the suspension thus prepared was dried by means of a nozzle atomizer, with an inlet temperature and an outlet temperature of the atomizer equal to 400°C and 120°C, respectively. The alumina obtained (in particle forms) is labeled AL1.

#### EXAMPLE 2

A composition according to the invention was prepared:

- a) to do this, the alumina AL1 prepared in example 1 was put back into suspension in water so as to obtain a 58 g/l suspension of  $\text{Al}_2\text{O}_3$ ;
- b) in addition, example 12 of patent application EP 0 520 862 was used, but without the spray drying step. Thus, the precipitated silica slurry obtained in example 1 of patent application EP 0 520 862 was filtered and washed by means of a filter-press in such a way that a silica cake having a loss on ignition of 79% (and therefore a solids content of 21% by weight) was recovered. This cake was then



fluidized by mechanical and chemical action (addition of the amount of sodium aluminate corresponding to an Al/SiO<sub>2</sub> weight ratio of 3000 ppm); after this disintegration operation, a suspension of precipitated silica (in the form of a pumpable cake) having a pH of 6.3 was obtained;

c) next, 0.99 liters of the alumina suspension obtained in a) were stirred for 10 minutes in a Rayneri stirrer fitted with a defloculating blade, at a speed of 2000 rpm; the pH of the suspension was 3.2. In parallel, 1 liter of water was added to 713 g of the precipitated silica suspension obtained in b) and the suspension thus prepared was also stirred, for 10 minutes, in a Rayneri stirrer fitted with a defloculating blade at a speed of 2000 rpm;

d) the precipitated silica solution obtained in c) was rapidly added to the alumina suspension obtained in c), with mechanical stirring (Rayneri Turbo test 200). The mixture was stirred for 15 minutes (2000 rpm). The suspension obtained had a pH of 3.7;

e) the suspension prepared in d) was dried by means of a nozzle atomizer, with an inlet temperature and an outlet temperature of the atomizer of 400°C and 120°C, respectively. The composition obtained is labeled C1.

EXAMPLE 3

Two polymer compositions were prepared:

- one containing composition C1 according to the invention (composition 1);
- the other containing a direct blend of the alumina AL1 and of the precipitated silica (labeled MP1) obtained after example 12 of the patent application EP 0 520 862 (control composition R).

**Table 1**

(compositions in parts by weight)

	Composition 1	Composition R
SBR <sup>(1)</sup>	100	100
C1	50	0
AL1	0	12.5
MP1	0	37.5
Silane Si69 <sup>(2)</sup>	4	4
Diphenylguanidine	1.45	1.45
Stearic acid	2.5	2.5
Zinc oxide	2.5	2.5
Antioxidant <sup>(3)</sup>	1.45	1.45
Sulfenamide <sup>(4)</sup>	2	2
Sulfur	1	1

(1) Styrene-butadiene copolymer synthesized in solution (BUNA VSL 5525-1 type) containing 27.3%

oil;

- (2) Filler/polymer coupling agent (sold by Degussa);
- (3) N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine;
- (4) N-cyclohexyl-2-benzothiazyl sulfenamide.

The compositions were prepared by working the elastomers thermomechanically in an internal mixer (Brabender type) having a volume of 70 cm<sup>3</sup>, in two steps, with a mean blade speed of 80 revolutions per minute until a temperature of 110°C was obtained, these steps being followed by a finishing step carried out on an external mixer.

The vulcanization of the compositions was tailored to the vulcanization kinetics of the corresponding mixes.

The properties of the compositions are given below, the measurements having been made (on the vulcanized compositions) according to the following standards and/or methods:

#### Rheological and vulcanization properties

- Mooney viscosity: NF T 43005 standard (measurement of Mooney Large (1 + 4) at 100°C, using a Mooney viscometer);

- Vulcanization: NF T 43015 standard.

A Monsanto 100 S rheometer was used, especially for the minimum torque ( $C_{\min}$ ) and maximum torque ( $C_{\max}$ ) measurement:

- $T_{s2}$  corresponds to the time over which it is possible to monitor the mix - the rubber mix cures after  $T_{s2}$  (start of vulcanization);
- $T_{90}$  corresponds to the time at which 90% of the vulcanization has taken place.

#### Mechanical properties

- Tensile properties (moduli, elongation at break, tensile strength): NF T 46002 standard.

The x% moduli correspond to the stress measured at a tensile elongation of x%.

- Tear strength: DIN 53-507 standard.
- Shore A Hardness: ASTM D2240 standard

The value in question is determined 15 seconds after application of the force.

#### Mechanical properties (Payne effect)

The real modulus ( $G'$ ), the imaginary modulus ( $G''$ ) and the loss tangent ( $\tan\delta$ ), defined as the ratio of  $G''$  to  $G'$ , were measured at various strain rates on a mechanical spectrometer (Viscoanalyzer VA2000 from Metravib RDS).

The test conditions were the following:

The test samples were of parallelepipedal shape (length: 6 mm; width: 4 mm; thickness: 2.5 mm, approximately). A sinusoidal strain of increasing amplitude was applied at a constant frequency of 5 Hz.

$G'$ ,  $G''$  and  $\tan\delta$  were determined at each strain rate. In the table below,  $\Delta G'$  refers to the difference between the measured modulus  $G'$  at a shear strain of 0.001 and the measured modulus  $G'$  at a shear strain of 1 and  $\tan\delta_{\max}$  corresponds to the maximum of the loss tangent as a function of strain.

Table 2

	Composition 1	Composition R
Mooney Viscosity	60	43
Vulcanization:		
$C_{\min}$ (in.lb)	10.9	7.4
$T_{82}$ (min)	12	10
$T_{90}$ (min)	41	39
$C_{\max}$ (ln.lb)	72	69
Mechanical properties:		
100% Modulus (MPa)	2.6	2.6
300% Modulus (MPa)	11.1	9.9
Elongation at break (%)	490	460
Tensile strength (MPa)	20.8	17.9
Tear strength (kN/m)	16.8	10.5
Shore A Hardness	67	64
Dynamic properties (Payne effect):		
$\Delta G'$ (MPa)	11.3	6.8
$\tan\delta_{\max}$	0.53	0.49

It may be seen that there is a much better compromise of properties in composition 1 according to the invention than the control composition R.

In addition, comparison between the photographs obtained in scanning electron microscopy of the two compositions showed that no agglomerate or aggregate was detectable in composition 1 according to the invention, whereas the presence of agglomerated objects of about ten microns in diameter was observed in the case of the control composition R; the quality of the macrodispersion of alumina in the polymer composition was substantially improved in the case of composition 1 according to the invention.

#### EXAMPLE 4

The following reactants were introduced into a static mixer (Lightnin) with the concentrations and flow rates indicated below:

- aluminum sulfate (22.75 g/l - 500 l/h)
- sodium aluminate (290 g/l - 86 l/h)

The temperature was maintained at 60°C.

On leaving the static mixer, the pH was 9 and the aluminum monohydrate concentration obtained was 60 g/l.

Next, the monohydrate was put into a reactor (volume: 12 l) containing a stirring system consisting of a propeller, the stirring power being 500 W/m<sup>3</sup>.

Sodium aluminate (concentration: 290 g/l) was added to the reactor in order to maintain the pH at 9 at 90°C, at which temperature the mix was left to age.

for 3 hours.

The alumina after the aging step was then filtered, washed and dried, as in example 1.

The alumina obtained (labeled AL2) had the following characteristics:

- the dominant crystalline form: boehmite;
- degree of crystallinity: 85%;
- crystallite size: 45 Å.

#### EXAMPLE 5

A composition according to the invention was prepared:

a) to do this, 491 g of alumina AL2 prepared in example 4 was put back into water so as to obtain 1 liter of suspension;

b) in addition, example 12 of patent application EP 0 520 862 was used, but without the spray drying step. Thus, the precipitated silica slurry obtained in example 1 of patent application EP 0 520 862 was filtered and washed by means of a filter-press in such a way that a silica cake having a loss on ignition of 79% (and therefore a solids content of 21% by weight) was recovered. This cake was then fluidized by mechanical and chemical action (addition of an amount of sodium aluminate corresponding to an Al/SiO<sub>2</sub> weight ratio of 3000 ppm); after this disintegration operation, a suspension of precipitated



silica (in the form of a pumpable cake) having a pH of 6.3 was obtained;

c) next, the suspension obtained in a) was stirred for 10 minutes in a Rayneri stirrer fitted with a defloculating blade, at a speed of 2000 rpm; the pH of the suspension was 11. In parallel, 1 liter of water was added to 713 g of the precipitated silica suspension obtained in b) and the suspension thus prepared was also stirred, for 10 minutes, in a Rayneri stirrer fitted with a defloculating blade at a speed of 2000 rpm;

d) the precipitated silica solution obtained in c) was rapidly added to the alumina suspension obtained in c), with mechanical stirring (Rayneri Turbo test 200). The mixture was stirred for 15 minutes (2000 rpm). The suspension was then diluted so that its final volume was 4 liters. The suspension obtained had a pH of 8.2;

e) the suspension prepared in d) was dried by means of a nozzle atomizer, with an inlet temperature and an outlet temperature of the atomizer of 400°C and 120°C, respectively. The composition obtained is labeled C2.

#### EXAMPLE 6

Two polymer compositions were prepared as in example 3:

- one containing composition C2 according to the invention (composition 2);

- the other containing a direct blend of alumina AL2 and precipitated silica (labeled MP1) obtained after example 12 of patent application EP 0 520 862 (control composition R').

**Table 3**

(compositions in parts by weight)

	Composition 2	Composition R'
SBR <sup>(1)</sup>	100	100
C2	50	0
AL2	0	12.5
MP1	0	37.5
Silane Si69 <sup>(2)</sup>	4	4
Diphenylguanidine	1.45	1.45
Stearic acid	2.5	2.5
Zinc oxide	2.5	2.5
Antioxidant <sup>(3)</sup>	1.45	1.45
Sulfenamide <sup>(4)</sup>	2	2
Sulfur	1	1

(1) Styrene-butadiene copolymer synthesized in solution (BUNA VSL 5525-1 type) containing 27.3% oil;

(2) Filler/polymer coupling agent (sold by Degussa);

- (3) N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine;  
 (4) cyclohexyl-2-benzothiazyl sulfenamide.

The properties of the compositions are given below, the measurements having been carried out (on the vulcanized compositions) according to the standards and/or methods indicated above.

**Table 4**

	Composition 2	Composition R'
Mooney Viscosity	40	49
Vulcanization:		
C <sub>min</sub> (in.lb)	8.1	8.2
T <sub>S2</sub> (min)	5	6
T <sub>90</sub> (min)	40	32
C <sub>max</sub> (ln.lb)	68	67
Mechanical properties:		
100% Modulus (MPa)	2.8	2.2
300% Modulus (MPa)	10.8	10.1
Elongation at break (%)	470	450
Tensile strength (MPa)	19.5	17.7
Tear strength (kN/m)	10.6	6.6
Shore A Hardness	65	63
Dynamic properties (Payne effect):		
$\Delta G'$ (Mpa)	9.1	5.1
$\tan\delta_{\max}$	0.56	0.49

Likewise, it may be seen that composition 2 according to the invention has a much better compromise of properties than the control composition R'.

In addition, comparison between the photographs obtained in scanning electron microscopy of the two compositions showed that no agglomerate or aggregate was detectable in composition 2 according to the invention, whereas the presence of agglomerated objects of about ten microns in diameter was observed in the case of the control composition R'; the quality of the macrodispersion of alumina in the polymer composition was substantially improved in the case of composition 2 according to the invention.